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INTERPRETATION AND APPLICATION OF ELECTROKINETIC PHENOMENA

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INTERPRETATION AND APPLICATION OF ELECTROKINETIC PHENOMENA

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Synopsis The parallels between ionic transport, electrophoresis and electro-osmosis are briefly discussed. It is pointed out that the interpretation of the electrophoretic mobility cannot be based on charge and friction constant alone. The flow and the distortion of the ionic atmosphere (electric double layer) cause in nearly all circumstances a large retardation.

The zeta potential is defined as the potential at the surface between the freely mobile liquid and the liquid firmly adhering to the particle surface. It is a useful notion when the particle surface is well defined, much less useful in the case of polyelectrolytes or highly swollen structures. Electrolytes compress ionic atmospheres and double layers and thereby cause a decrease of the electrokinetic mobility and the zeta potential.

The electrokinetic mobility can be used to obtain information on the charge of particles and from that to estimate electrostatic repulsion or attraction. Here again the effect is determined by charge *and* electrolyte content, not by charge or zeta potential alone. Direct applications of electrokinetic phenomena are drying by electro-osmosis, electrodeposition on electrodes, accumulation on a membrane or filter, orientation of fibres and plates, separations based on differences in mobility.

1—*Introduction*

WHEN an electric field is applied to an electrolyte solution, ions move in accordance with their charge and their coefficient of friction. A similar motion is observed in suspensions of particles that carry an electric charge. This motion is called *electrophoresis*. When the concentration of particles is made higher and higher until the particles are in contact with each other and with the walls of the container, they form an immobilised plug. If an electric field is applied now the particles cannot move, but the liquid moves with respect to the particles. This phenomenon is called *electro-osmosis*.

Electrophoresis and electro-osmosis are both electrokinetic phenomena in which two phases move relative to one another under the influence of an

Under the chairmanship of A. A. Robertson electric field parallel to their interface. We shall not discuss here the other group of electrokinetic phenomena, such as streaming current or sedimentation potential in which mutual displacement of two phases is the cause of an electric current or of a potential difference.

The velocity of an ion in solution is not completely described by the simple relation

$$\text{charge} \times \text{field strength} = \text{velocity} \times \text{friction constant} \quad . \quad . \quad (1)$$

The presence of the other ions generally leads to a lower velocity than that of an isolated ion. The theory of these influences has been given by Debye and Hückel,(1) Onsager(2) and has been refined by several later authors. Descriptions of these theories can be found in textbooks of physical chemistry (e.g. Moore(3)) and in more detail in textbooks of electrochemistry (e.g. MacInnes,(4) Kortüm(5)). Interionic attractions and repulsions build up an ionic atmosphere around each ion. By their displacement opposite to that of the central ion and by their distortion in the electric field these ionic atmospheres cause an *electrophoretic retardation* and a *time of relaxation retardation* respectively.

The same effects occur with suspended particles, but they are quantitatively more important than with ions, because under most circumstances the extension of the ionic atmosphere is much larger than the size of an ion, whereas the atmosphere around a particle—usually called *electric double layer*—is often thinner than the particle diameter.

With ions there is usually little doubt about the magnitude of their charge, but with particles the situation is more complicated. A layer of one or a few solvent molecules adheres firmly to the particles and may be thought to be separated from the bulk of the liquid by a more or less well defined *slipping plane* or *surface of shear*. A part of the double layer may be contained in the adhering layer of solvent. Then the *electrokinetic charge* is the net charge inside the surface of shear, and the *electrokinetic potential* or *zeta-potential* is the potential at this surface.

The notion of the ζ-potential is useful in the case of massive particles with a well-defined impenetrable surface, but loses a good deal of its meaning with polyelectrolytes and with swollen gels.

2—*The structure of ionic atmospheres and of electric double layers*

BEFORE treating the electrophoresis of particles of various shapes, it is instructive to deal briefly with the structure of ionic atmospheres and of electric double layers.

The charge of a particle or of an ion attracts ions of opposite sign, called *counter ions*, and repels ions of its own sign, called *co-ions*. The average distribution of ions in such an atmosphere obeys *Boltzmann's law*,

$$n_i = n_{io} \exp(-z_i e\phi/kT), \qquad (1a)$$

$$c_i = c_{io} \exp(-z_i F\phi/RT). \qquad (1b)$$

Here n_i is the local average number of ions of type i per unit volume, n_{io} is the overall average for these ions, z_i is their charge number with sign included (-2 for SO_4^{2-}), e is the elementary charge, ϕ is the local potential (the average potential or the potential far away from any particles is zero), k is Boltzmann's constant and T the absolute temperature. Further c_i and c_{io} are the local and the average concentration of the ions, i, resp., F is the Faraday constant, and R the gas constant.

The relation between the potential, ϕ, the distance from the centre and the local charge density, ρ, is given by Poisson's law which, in the four quantity nationalised system is written

$$\text{div grad}\,\phi = \nabla^2\phi = -\frac{\rho}{\varepsilon\varepsilon_0}, \qquad (2a)$$

where ε_0 is the permittivity of the vacuum and ε is the dielectric constant of the solution. In the classical three quantity, non-rationalised, system, Poisson's law reads:

$$\nabla^2\phi = -\frac{4\pi\rho}{\varepsilon}. \qquad (2b)$$

With

$$\rho = \sum z_i n_i e = \sum z_i c_i F, \qquad (3)$$

equations (*1*) and (*2*) can be combined to the *Poisson–Boltzmann equation:*

$$\nabla^2\phi = -\frac{1}{\varepsilon\varepsilon_0} \sum_i z_i F c_{io} \exp(-z_i F\phi/RT). \qquad (4)$$

This equation can be solved, leading to a description of ϕ and c_i (or n_i) as a function of the distance from the centre, when the electroneutrality condition,

$$\text{total charge in the solution} + \text{total charge of particle (or ion)} = 0 \qquad (5)$$

is used.

When ϕ is small ($z_i\phi < 25$ mV) the exponentials in (*1*) and (*4*) may be expanded and only the first two terms retained. This leads to

$$\nabla^2\phi = -\frac{\sum z_i F c_{io}}{\varepsilon\varepsilon_0} + \sum \frac{z_i^2 F^2 c_{io}}{\varepsilon\varepsilon_0 RT}\phi = \kappa^2\phi, \qquad (6)$$

with

$$\kappa^2 = \frac{F^2 \sum_i z_i^2 c_{io}}{\varepsilon\varepsilon_0 RT} = \frac{2F^2 I}{\varepsilon\varepsilon_0 RT} \qquad (7)$$

or

$$\frac{1}{\kappa} = \left(\frac{\varepsilon\varepsilon_0 RT}{2F^2}\right)^{1/2} \cdot \frac{1}{\sqrt{I}} = \frac{0{\cdot}3038\ \text{nm}}{\sqrt{I\,mol^{-1}\,l}}, \quad . \quad . \quad . \quad . \qquad (8)$$

where I is the ionic strength, $I = \frac{1}{2}\sum c_{io}z_i^2$, and the electroneutrality of the solution requires that $\sum_i z_i F c_{io} = 0$. The numerical value is valid for water ($\varepsilon = 78{\cdot}3$) at 25° C.

Equation (*6*) (and similarly the more complete equation (*4*)) can be solved leading to

$$\phi = \phi_0 \exp(-\kappa x) \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

for the potential at a distance x from a flat surface charge with potential ϕ_0 and to

$$\phi = \phi_0 \frac{\exp \kappa(a-r)}{r/a} = \frac{Q}{4\pi\varepsilon\varepsilon_0} \frac{\exp \kappa(a-r)}{r} \quad . \quad . \quad . \quad . \qquad (10)$$

for the potential at a distance r from the centre of a sphere with radius a, surface potential ϕ_0, and charge Q.

One of the most important aspects of the above developments is the occurrence of the quantity κ in equation (*6*) and following. $1/\kappa$ (equation (*8*)) is a length; it indicates the order of magnitude of the spatial extension of ionic atmospheres quite independent of the number and spatial arrangement of the charges on the particles. As a matter of fact often quite a reasonable first approximation of thermodynamic and hydrodynamic phenomena involving charged particles is obtained by assuming the whole counter charge to be located at a distance, κ^{-1}, from the charge(s) on the particle. It is therefore useful to give a small table of values of $1/\kappa$ (Table 1).

TABLE 1—Values of $1/\kappa$, the 'thickness of the ionic atmosphere', for monovalent electrolytes in water at 25° C. For a solvent with dielectric constant ε, the figures should be multiplied by $(\varepsilon/78{\cdot}3)^{1/2}$. For an electrolyte of the type $M_{v+}{}^{z+}A_{v-}{}^{z-}$ the figures should be divided by $[(v_+z_+{}^2+v_-z_-{}^2)/2]^{1/2}$

c in mol l^{-1}	*1/*κ *in nm*
10^{-5}	96
10^{-4}	30
10^{-3}	9·6
10^{-2}	3·0
10^{-1}	0·96
1	0·30

3—*Electrophoresis of massive particles*

ALTHOUGH one might argue that cellulose fibres should be treated as cylinders or perhaps as polyelectrolytes or swollen gels, we shall nevertheless

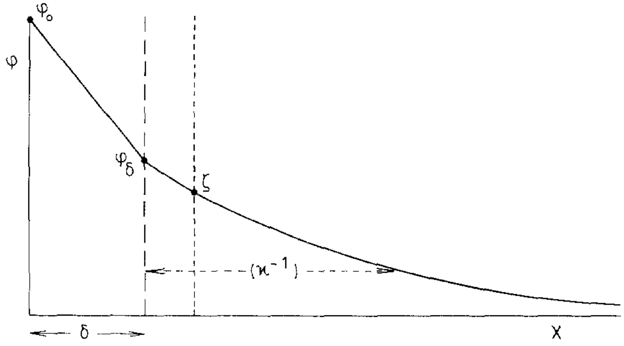


Fig. 1—Potential, ϕ, against distance, x, from the particle surface

start the discussion with the electrophoresis of massive spherical particles because this is by far the most completely investigated case and it forms a good introduction to the more complicated cases.

3.1—*Spherical particle*

We consider the electrophoresis of a single solid spherical particle in an electrolyte solution. This should be representative for the behaviour of a dilute suspension in which the particles are separated by distances, many times κ^{-1}. The particle has acquired a charge at its surface by adsorption of ions or by dissociation of surface groups. If the surface charge density is not too low (and mobile on the surface) we may consider it as being smeared out to a constant surface charge density.

For that case the solution of the linearised Poisson–Boltzmann equation is given by equation (*10*). Loeb, Wiersema and Overbeek(6) have given exact numerical solutions for the non-linearised Poisson–Boltzmann equation (*4*) around a sphere. In these solutions and in equation (*10*) it is assumed that dissolved ions can come infinitely close to the surface of the particle. In reality the ions with their solvation shell have a finite size. Stern(7) has indicated how this finite size can be taken into account by assuming a layer of thickness, δ, (*Stern layer*) to be free of charge. The course of the electric potential with distance is then as given in Fig. 1.

With this model we have to distinguish the surface potential, ϕ_0, the Stern potential, ϕ_δ, and the ζ-potential at the surface of shear, which we have drawn arbitrarily slightly beyond the Stern plane.

In Fig. 2 we give a schematic picture of the particle (radius a, including the

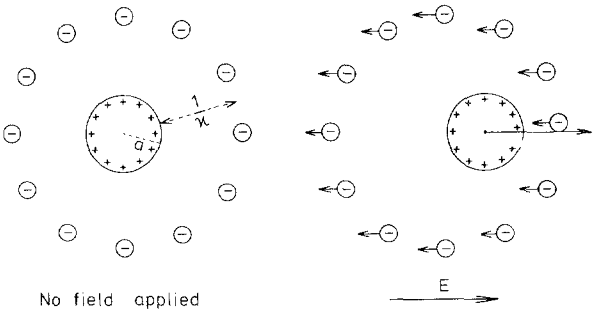


Fig. 2—Spherical particle with double layer with and without applied field

adhering solvent layer) with its atmosphere concentrated at a distance, κ^{-1}, from the surface in rest and with an electric field, E, applied.

In the absence of any double layer influence the velocity, v, of the particle in the field, E, would be

$$v = \frac{QE}{6\pi\eta a}, \qquad (11)$$

where η is the viscosity of the liquid. The influence of the electrophoretic retardation can be easily taken into account. The counterions will move through the liquid in a direction opposite to that of the particle. They transfer their momentum to the surrounding liquid and if we disregard the distortion of the double layer the liquid inside the double layer will move as a sphere with radius $a+\kappa^{-1}$ and a charge, $-Q$. The net velocity of the particle will be the difference of its own velocity and that of the double layer. Thus

$$v = \frac{QE}{6\pi\eta a} - \frac{QE}{6\pi\eta(a+\kappa^{-1})} = \frac{\varepsilon\varepsilon_0\zeta E}{1{\cdot}5\eta} \qquad (12a)$$

or in the non-rationalised three quantity system

$$v = \frac{\varepsilon\zeta E}{6\pi\eta}. \qquad (12b)$$

In the transition from Q to ζ in equation (*12a*) the relation

$$\zeta = \frac{Q}{4\pi\varepsilon\varepsilon_0 a} - \frac{Q}{4\pi\varepsilon\varepsilon_0(a+\kappa^{-1})} \qquad (13)$$

has been used.

The relation (*12a*) or (*12b*) between v and ζ remains exact, also if the diffuse nature of the double layer is taken into account (cf. Overbeek and Wiersema(8)).

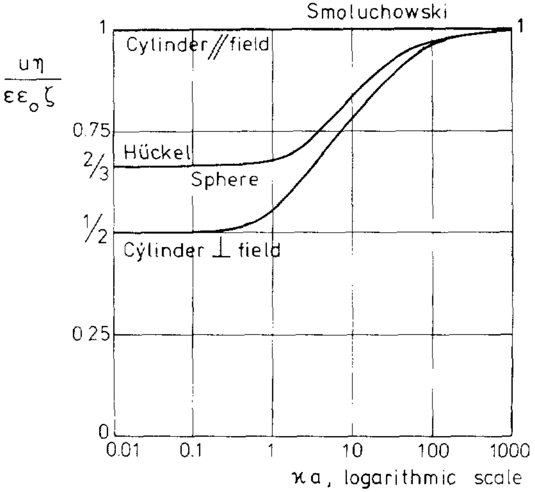


Fig. 3—Henry's results for the electrophoresis of spherical and cylindrical particles. The mobility, $u = v/E$

In the original derivations for the electrophoretic velocity by Helmholtz(9) and by von Smoluchowski(10) the factor 6π in equation (*12b*) was replaced by 4π. This was shown by D. C. Henry(11) to be due to the fact that the applied field is distorted by the presence of the particle. This distortion affects the mobility of the double layer strongly if it is thin ($\kappa^{-1} \ll a$, case considered by Helmholtz and Smoluchowski), but hardly at all if it is thick ($\kappa^{-1} \gg a$, case considered by Hückel(12)). Henry bridged the gap and gave equations for the electrophoretic velocity at the whole range of values of κa. His results for spheres and cylinders (see below) are shown in Fig. 3.

So far we have neglected the distortion of the ionic atmosphere. This distortion arises because in the electric field the ions of the atmosphere move away from their average equilibrium position and it requires some time (the relaxation time of the electrolyte solution) before the atmosphere is formed again. In the stationary state the atmosphere lags always somewhat behind and thus is the cause of a retarding electric field. This relaxation field has little influence on the electrophoretic mobility at very low and at very high κa, and for low ζ at any κa, but at intermediate values of κa it may be quite important since it increases more than proportionally with ζ.

The exact calculation of this time of relaxation effect is difficult. Approximations have been given by Booth(13) and by Overbeek(14). A complete numerical calculation has been performed by Wiersema *et al.*(15)

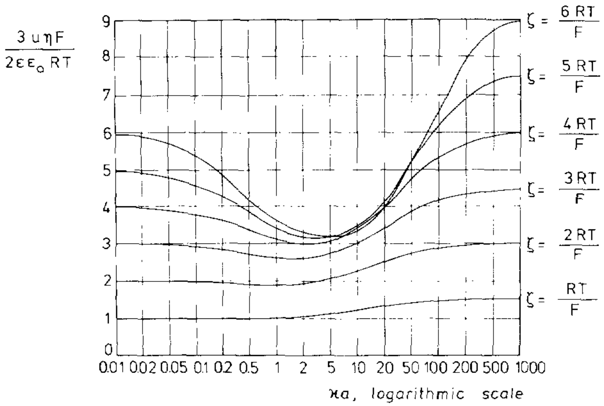


Fig. 4—Electrophoretic mobility of a sphere, expressed as a dimensionless quantity as a function of κa and ζ, if the relaxation effect is taken into account. The electrolyte is supposed to be uni-uni-valent. For other valencies and the influence of ionic mobilities see reference 15

We derive Fig. 4 from their publications.

Summarising we may state that for spherical particles exact relations between electrophoretic mobility u, surface charge, and zeta-potential are available, but only as the result of complicated numerical computations and only for a relatively limited range of potentials, charge numbers and mobilities of the ions. For low charges and potentials u is proportional to ζ. For high ζ and intermediate κa, u appears to reach a fairly low maximum value.

3.2—*Cylindrical particle*

The theoretical treatment of the electrophoresis of cylindrical particles is more complicated than that of spheres for several reasons and solution of the problems involved has been slow.

Henry(11) observed already that the angle between the cylinder axis and the field influences the electrophoretic velocity. For a cylinder parallel to the field the electrophoretic mobility is

$$u_{\parallel} = \frac{\varepsilon\varepsilon_0\zeta}{\eta}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

independent of κa (a is the radius of the cylinder). For a cylinder perpendicular to the field, $u_{\perp}$ depends on κa

$$u_{\perp} = \frac{\varepsilon\varepsilon_0\zeta}{\eta} f(\kappa a), \qquad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where $f(\kappa a) = 0{\cdot}5$ for $\kappa a \rightarrow 0$ and $f(\kappa a) = 1$ for $\kappa a \rightarrow \infty$. Gorin(16) calculated $f(\kappa a)$ for intermediate values of κa. They are shown in Fig. 3. De Keizer *et* *al.*⁽¹⁷⁾ showed that for random orientation the average mobility is

$$u_{\text{average}} = \tfrac{2}{3}u_{\perp}+\tfrac{1}{3}u_{\parallel}. \qquad (16)$$

This u_{average} would then be quite close (but not identical) to u_{sphere}, as can be seen in Fig. 3. The above equations neglect end effects and the relaxation effect and in equation *(15)* $f(\kappa a)$ is only independent of ζ for low potentials. For high surface potentials and surface charges the complete Poisson–Boltzmann equation has to be used. This can only be done numerically, but Philip and Wooding⁽¹⁸⁾ give a useful set of analytical approximations. Van der Drift⁽¹⁹⁾ has used these analytical equations, together with Henry's original development⁽¹¹⁾ to derive relations between the electrophoretic mobility, u_{average}, κa, and the charge per unit length of the cylinder.

This still does not include the relaxation effect.

Van der Drift,⁽¹⁹⁾ in the interpretation of the electrical transport in solutions of alkalipoly (methacrylates), used an empirical estimate, proposed by Möller *et al.*,⁽²⁰⁾ for the relaxation effect, which in his example lowered the electrophoretic mobility by 30–50 per cent. Recently Stigter⁽²¹⁾ has announced a theoretical calculation of the relaxation effect for cylinders.

Conclusion: The interpretation of the electrophoresis of cylindrical particles is still in development, although final results appear to be near. At this moment one may confidently use Henry's and Gorin's (slightly corrected by Stigter) results as long as the charge density and surface potentials are low and even for high surface potentials the relaxation effect may be neglected if κa is large (*vide infra*).

3.3—*Particles of arbitrary shape*

Considering the difficulties just mentioned for cylinders it would seem rather hopeless to interpret the electrophoresis of particles of more complicated shape.

The situation, however, is more favourable than might be expected at first sight. Looking again at Fig. 3 we see that all three curves merge to $u\eta/\varepsilon\varepsilon_0\zeta = 1$ for large κa. This is the old Smoluchowski limit derived by him for arbitrary shape, provided that the double layer is thin compared to any particle dimension and that it is not distorted in the field. Overbeek⁽²²⁾ could show that indeed in the limit of a thin double layer the relaxation effect due to the distortion of the double layer is so small, that it may be neglected. At the other extreme (double layer dimensions very much larger than those of the particles) the situation is simple again. The electrophoretic mobility is then given by

$$u = \frac{Q}{f}, \qquad (17)$$

where Q is the charge of the particle and f its friction coefficient, electrophoretic retardation and relaxation effect both being negligible. In aqueous suspensions it is difficult to reach this limit of a very thick double layer, but in nonaqueous, especially nonpolar, media the ionic concentration may be so low that the case, $\kappa a \ll 1$, may be quite realistic even for micron size particles.

4—*Electro-osmosis*

THERE are at least two reasons why we should be interested in electro-osmosis. In the first place in electrophoresis experiments the suspension is always contained in a cell or vessel. The electric field causing electrophoresis also generates an electro-osmotic flow along the walls of the container and the particles are subjected both to electrophoresis and electro-osmotic flow. Especially in microscopic electrophoresis or paper electrophoresis the correction for electro-osmosis must be made with care.

In the second place wet paper or wet porous plugs of cellulose fibres offer nearly ideal circumstances for studying electro-osmosis and perhaps for application. In many cases in which electro-osmosis occurs the thickness of the double layer is small compared to the dimensions of the vessel, the pores or even the fibres forming the plug. Consequently we are in the situation of large κa (a is any relevant dimension of vessel or plug) and thus the electro-osmotic mobility is described by equation (*14*).

This is a good point to come back to the remark that in electrophoresis equation (*14*) is the correct one to use for thin double layers irrespective of particle shape. Since the solution is a much better conductor than the particles or the material of the plug or the vessel, the applied electric field is distorted in such a way, that it is parallel to the interface. (Even if the particles are made of conducting material, a very slight polarisation stops the current from flowing through the particle.) A simple relation can then be derived between the local electric field and the local flow of the liquid. Consider a small part of the interface that may be taken as flat compared to κ^{-1}. Call the co-ordinate perpendicular to that interface x, the positive direction pointing into the liquid and taking $x = 0$ at the surface of shear. Then the stationary state after the application of an electric field requires that

$$\eta \frac{d^2v}{dx^2} = -E\rho = +E\varepsilon\varepsilon_0 \frac{d^2\phi}{dx^2}. \qquad (18)$$

Here v is the velocity in the liquid parallel to the interface, E the local field strength also parallel to the interface and ρ the space charge density. Integration with the boundary conditions that far away (far compared to κ^{-1}) from the interface $dv/dx = 0$, $\phi = 0$ and $d\phi/dx = 0$ and at the surface of shear

$v = 0$ and $\phi = \zeta$ leads to

$$\eta v^{\infty} = -E\varepsilon\varepsilon_0\zeta \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

or

$$u = \frac{v^{\infty}}{E} = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}, \quad . \quad . \quad . \quad . \qquad (20)$$

where v^{∞} is the local velocity in the liquid 'just outside the double layer' and considering the particle or plug as not moving. The minus sign indicates that with a negative ζ potential and thus a positive space charge the liquid flows down stream with E. In the absence of pressure gradients then anywhere in the solution far from the double layers the relation between local velocity and local field strength is given by equation (*20*). Thus equation (*20*) gives 'the' electro-osmotic mobility and with the sign reversed the mobility of a suspended particle in a stationary liquid.

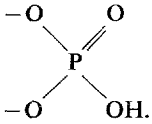
The main and important point is that electro-osmosis and electrophoresis are governed by similar equations and that these equations are identical (but for the sign) in the case of large κa.

5—*Electrophoresis of polyelectrolytes and swollen gels*

5.1—*Polyelectrolytes*

Polyelectrolytes consist of molecules containing a large number of ionisable groups, such as

$-$COOH or



Many biopolymers (proteins, nucleic acids) and synthetic (polyacrylates) or semisynthetic (carboxymethylcellulose, CMC) macromolecules belong to this category. Most polyelectrolytes are linear, rarely rigid rods, but usually either systematically coiled and folded (proteins) or coiled to a flexible rodform (nucleic acids) or simply forming a rather open random coil (CMC, polyacrylate). To explain the electrophoretic mobility of the flexible rods and random coils two models have been in use. In the *porous sphere model* the charges of the polyion are supposed to be homogeneously distributed in a sphere. The counterions and co-ions are distributed inside and outside this sphere according to the Poisson–Boltzmann equation. In the other model the polyion is *supposed to be a cylinder*, with a homogeneous surface charge. The small ions are distributed as discussed in section 3.2 in the space outside a suitably chosen cylinder radius a. The cylinder is assumed to be sufficiently

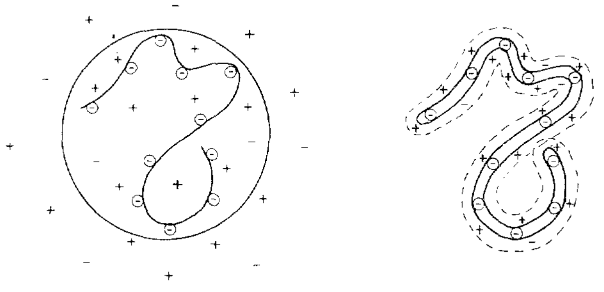

a. Porous Sphere b. Coiled Cylinder

Fig. 5—Models for polyelectrolytes

coiled, so that all orientations in space occur with equal probability, but open enough, so that interactions between two parts of the cylinder may be neglected. Fig. 5 gives a schematic picture of both models.

Electrophoresis equations for both models have been worked out. The porous sphere has been treated by Overbeek and Stigter(23) and by van Geelen(24) and by Hermans, Fujita and Napjus.(25–28) In these papers the relaxation effect is left out of consideration. Attempts to calculate this effect have been made by Longworth and Hermans(29) and by Imai and Iwasa(30) but their solutions are not readily applicable to practical cases. A good survey is given by van der Drift.(19)

It should be obvious that the choice between the two models of Fig. 5 should be determined by the ratio of the extension of the double layer and that of the coil. Quite often the model of the coiled cylinder is the more realistic one. This means that the electrophoresis equations of the randomly oriented cylinder as discussed in section 3.2, are relevant for polyelectrolytes. It is usually desirable to convert the zeta potentials into charges per unit length of the cylinder, since charge rather than potential at the surface of shear is usually what we know, or want to know about a polyelectrolyte molecule.

It may be useful to show here some of the data of van der Drift(19) on the electrophoretic mobility of polymethacrylate ions in salt solutions. Fig. 6 shows these mobilities for three different charge densities plotted against the square root of the electrolyte concentration. As mentioned earlier mobilities would be on the order of twice as high as they are now in the absence of a relaxation effect. The strong decrease of the mobility with increasing electrolyte concentration is mainly due to the electrophoretic retardation (hydrodynamic effect). Qualitatively this would occur in any reasonable model, quantitatively this decrease can be rather well explained on the basis of a

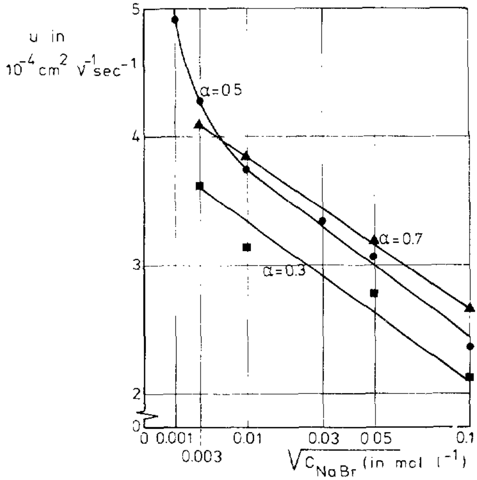


Fig. 6—Electrophoretic mobility, u, of polymethacrylate ions ($M \sim 160\,000$) in aqueous NaBr solutions at 25° C. The three lines correspond to three degrees of ionisation, $\alpha = 0{\cdot}3$, $\alpha = 0{\cdot}5$ and $\alpha = 0{\cdot}7$ resp. with a corresponding charge density of 1 elementary charge per 0·785, 0·47 and 0·335 nm resp.

cylinder model. The relatively weak influence of the charge density is also in agreement with this model.

5.2 *Swollen gels*

A GEL that shows electrokinetic phenomena is or can be considered as a crosslinked polyelectrolyte. If the degree of cross linking is weak and the gel is highly swollen the cylinder model as treated in the previous section may be adequate. But if the degree of crosslinking and the charge density are high, as in most ion exchange resins the model of a porous sphere briefly mentioned above may be more suitable. The size and the shape of the gel particle is only of importance if it is very small (not many times κ^{-1}). Otherwise shape and size are irrelevant. In that case the electrophoretic mobility (or in the inverse experiment the electro-osmotic mobility) is given by the simple equation

$$u = \frac{ze}{nf}, \qquad \ldots \ldots \qquad (21)$$

where z is the number of elementary charges e in a piece of gel, n the number of chain elements (e.g. monomers) in the same piece and f the friction coefficient of such an element when it is not disturbed by any other element.

This equation (*21*) expresses that the piece of gel behaves as completely freely drained because the counterions in the gel screen the different chain elements from one another.

In principle the electrolyte concentration in which the gel is embedded does not affect its mobility as long as the condition of high charge density (distance between charges $\ll \kappa^{-1}$) is satisfied.

6—*Influence of low charge density*

IN the preceding sections particle charges have been treated as if they were smeared out over the available surface. This is a reasonable model if the individual charges are separated by distances that are not large compared to the thickness of the ionic atmosphere. But what happens if the charge density becomes so low that each charge is surrounded by its own ionic atmosphere with little overlap between these separate ionic clouds?

Even in this case the ratio of particle size (a) and double layer thickness (κ^{-1}) determines whether the electrophoretic retardation is small or large and if at, say, $\kappa a = 10$ the electrophoretic retardation reduces the mobility by a factor of about 10 at high charge density the effect is similar at low charge density although in detail there may be some differences. Even a double layer that is only present patch wise has a strong influence on electrokinetics if it is close to the surface.

Consequently although detailed calculations on the electrokinetics of surfaces covered with a low number of elementary charges has not been carried through, extrapolation from what is known at high charge density and at the given ionic strength, will certainly lead to approximately correct answers. It is obvious that under those circumstances the ζ-potential lacks physical reality, although it may occur as a formal intermediate in the calculations.

7—*Origin of the particle charge*

THE charge of the particles stems from either of three sources or from a combination of them.

a. Adsorption of ions
b. Exchange of electrons with a redox reaction in the solution
c. Dissociation of ionisable groups fixed on the particles

The adsorption of ions may be divided into adsorption of potential determining ions (e.g. Ag^+ with Ag particles, Zn^{2+} and S^{2-} with ZnS particles, Fe^{3+}, H^+ and OH^- with FeOOH particles etc.) and adsorption of other ions (e.g. Cl^- on proteins, big organic ions such as soap ions on nearly any surface). Polyelectrolyte molecules are charged by dissociation of

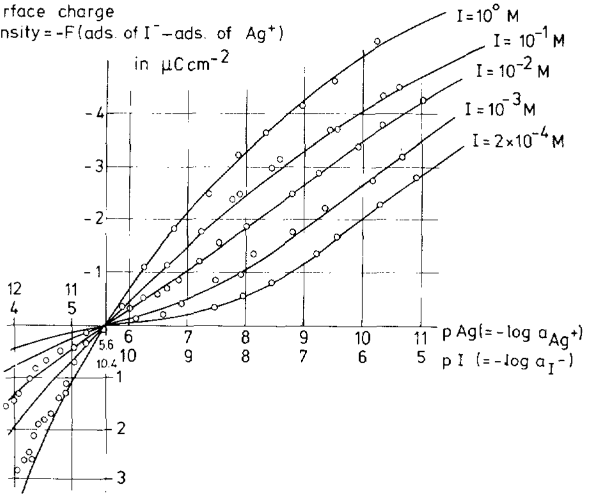


Fig. 7—Surface charge density of AgI in aqueous $NaClO_4$ solutions of various ionic strengths

$-COOH$, $-OSO_3H$, and other acidic groups or by taking up H^+ ions e.g. in the reaction $-NH_2+H^+ \rightarrow -NH_3{}^+$.

The degree of charging of the particles is determined by the activity of the relevant ions, by the standard free energy of adsorption (or dissociation) and finally by the surface potential obtained, since the work term ‘charge of ion times surface potential’ always works against further adsorption. In cases in which the adsorption or dissociation is not complete (saturated) the charge can be influenced by an unspecific change in ionic strength because the ionic strength affects the capacity of the electric double layer.

A good illustration is given by the adsorption of Ag^+ and I^- ions on AgI as a function of Ag^+ or I^- ion activity (linked by the solubility product) and the ionic strength (Fig. 7). The charge becomes more positive with increasing silver ion activity and more negative with increasing iodide ion activity. Positive and negative surface charges both increase with increasing ionic strength (compression of the double layer). Similar effects are found in the titration of polyelectrolytes with acid or base.

The charge of particles or polyions is practically independent of the ionic strength in cases where ionisation is nearly complete ($-COOH$ at high pH, $-OSO_3H$ or $-SO_3H$ at nearly all pH) or where the adsorption is nearly complete (high concentration of particles with high specific surface area in low concentrations of strongly adsorbed ions).

Cellulose, not being a metal, can only become charged by adsorption of ions or by dissociation. At very high pH the alcoholic OH groups dissociate to a measurable extent, but the charge at lower pH must be due to more strongly acidic groups such as $-COOH$ formed by oxydation of $-CH_2OH$ groups or of aldehydic end groups of the chain. Formation of ester groups with sulphuric acid might also lead to dissociated $-OSO_3^-$ groups. Furthermore the presence of noncellulosic contaminants such as pectic acid might contribute to the charge of the combination.

Intentional modification of cellulose (e.g. carboxymethylcellulose) may of course also be a source of charge.

8—*Use of electrophoretic data*

ONE of the more important uses of electrokinetic data is the determination of the *sign of the charge* and of the *point of zero charge* (circumstances under which the charge is zero). In this case the theory is quite simple; no relaxation effect; proportionality factor between charge, surface potential and mobility immaterial. Often electro-osmosis is a more suitable technique than electrophoresis because at and near zero charge suspensions lose their stability and tend to coagulate.

The next somewhat more complicated application is the calculation of *zeta potential and charge* from the mobility and the changes in these quantities brought about by addition of electrolytes and nonelectrolytes.

The zeta potential is then an important parameter in considerations on the *stability of suspensions*, because in many cases ζ is the nearest available approximation to the Stern potential, ϕ_δ (cf. Fig. 1). This Stern potential is one of the factors determining the electrostatic repulsion when two particles come close together. For spherical particles (radius a) at a distance, H, between the Stern planes, the free energy of repulsion, V_R, is approximately given by

$$V_R = 2\pi\varepsilon\varepsilon_0 a\phi_\delta^2 \exp(-\kappa H). \quad . \quad . \quad . \quad . \quad (22)$$

The repulsion is quite sensitive to the ionic strength, since the range of the repulsion (κ^{-1}) is decreased by adding electrolyte and moreover ϕ_δ (just as ζ) decreases strongly at higher κ.

The stability of a suspension (in the sense of noncoagulation) now depends on whether the repulsion as given in (*21*) is stronger or weaker than the always present van der Waals attraction. Numerical values are such that quite often the transition between stability and coagulation is found at intermediate electrolyte concentrations (say 0·01–0·1 molar).

In the same way ζ potentials are useful to estimate the electrostatic interaction between two *particles of different nature*, attraction if the surface charges have opposite sign, repulsion if they have the same sign, and—perhaps unexpectedly—attraction at very short distances even if the two charges have the same sign as long as their absolute values are sufficiently different. This field of *heterocoagulation* should certainly interest those working in the paper industry, where often particles of quite different nature are brought together.

Unfortunately there is no simple step from the ζ-potential to stability as was believed to be the case in Freundlich's days. The electrolyte concentration, leading to κ, particle size, a, and shape, have their own impact on the electrostatic interaction and thus on the stability.

If one wants to *compare interparticle forces to mechanical forces* applied from outside, it is good to remember that interparticle energies and forces are proportional to the particle radius, but shear forces are proportional to the square of that radius. Therefore, other circumstances being equal, small particles are less easily torn apart by shear than large ones. Particles held together by van der Waals attraction at a distance of a few Å must be quite a bit larger than 1 μ before they can be separated by a rate of shear of 1 000 $\sec^{-1}$ in water. But if electrostatic repulsion is present (equation *22*) this can overcome the van der Waals attraction partially or completely.(31)

For *polyelectrolytes* the mobility is often more difficult to measure because the particles cannot be made visible in the (ultra) microscope. On the other hand the charge per unit mass is usually so large, that it can be determined analytically. Therefore electrophoresis is not in the first place a tool to obtain information on polyelectrolytes. It remains as an important test of our understanding of the kinetics of polyelectrolytes. And, of course, in cases of an unknown polyelectrolyte, determination of the sign of the charge by electrophoresis can be extremely useful.

9—*Applications of electrophoresis and of electro-osmosis*

SEVERAL patents(32) have been given for the *drying* of peat by *electro-osmosis*. The wet peat is placed between two electrodes. On the application of a d.c. field water moves to one of the two electrodes and is eliminated by allowing it to drip off the electrode. The method, which is in principle applicable to many porous materials, and which seems to be attractive on account of the large mass of water moved per unit charge transported has never acquired widespread application, presumably because it was not economic. Still in certain cases perhaps even in the paper industry it might be worthwhile to reconsider its possibilities.

Electrodeposition has found widespread application. In this process particles suspended in an aqueous or non-aqueous liquid are deposited on an electrode on the application of a d.c. field. The process is an interesting combination of electrophoresis, which carries the particles towards the electrode and electrolysis which by generating electrolyte at the electrode causes the particles to precipitate.(33) Some of the practical advantages of the process are: favourable transported mass to charge ratio; even coverage of the electrode irrespective of its shape by a dense layer of particles, because the streamlines are concentrated towards parts of the electrode that are not yet covered; good adherance following the coagulation of the suspension after concentration near the electrode. The process is used for painting with latex—and other paints.

Also for covering metals with thin layers having special properties, such as thermal emission of electrons, insulation etc. The process might be extended to precipitate particles on or in porous layers such as paper. It could certainly be used to eliminate undesirable particles (also emulsion droplets) from suspensions.

Electrodialysis is a process in which a solution or suspension contained between two membranes is freed from electrolytes by the application of a d.c. electric field. It is not an electrokinetic process as such, but since in general suspended particles are electrically charged the particles are driven by electrophoresis towards one of the membranes. The high particle concentration at one membrane and the low concentration at the other membrane result in density differences, that start convection in the cell leading finally to a vertical separation of the suspension in a highly concentrated part at the bottom and a particle free solution at the top. This *electrodecantation*(34) or *electrophoresis convection*(35) can be a very efficient method for concentrating and purifying suspensions.

Electrophoresis as such has been used in many variants for the analysis and separation of mixtures of particles with different mobilities. Especially for proteins and other polyelectrolytes of biological interest paper- and gel-electrophoresis are about as important as the corresponding forms of chromatography. Also viruses and whole cells show quite specific electrophoretic mobilities, which can be used for characterisation and separation.

Elongated particles will be oriented with their long axis parallel to the applied field (*Kerr-effect*) if the field is sufficiently strong to overcome Brownian rotation. The orientation occurs because the deformation of the double layer (relaxation effect) makes the particle into a dipole with the dipole axis in the direction of the long axis of the particle. The effect might find practical applications.

The above was written in the conviction that electrophoresis and electro-osmosis are important characteristics of particles and surfaces. The point was stressed that the interpretation is not only based on particle charge and surface potential, but that electrolyte concentration and to a lesser extent shape have also to be considered. In the last few sections a number of actual and potential applications of electrokinetics have been mentioned.

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Discussion

Mr T. Lindström How does the sign of the charge of the particle enter calculation of the thickness of the electrostatic double layer when we are comparing for example sodium sulphate and calcium chloride? I would expect that if we have calcium chloride, this electrolyte would be more efficient in screening for example the charge of a negative particle.

Prof. J. T. G. Overbeek Yes, that is quite correct. As far as I have given equations they are only applicable to low surface charge and low surface potentials, and as soon as the surface potential gets high the stronger attraction of multivalent ions of opposite sign makes itself felt very much more pronouncedly. Just to give one example, you can flocculate a negatively charged suspension with one tenth molar of 1:1 electrolyte or with about 1 milli-molar 2:1 electrolyte (barium chloride). You will need 50 milli-molar of sodium sulphate to do the trick, since the sulphate isn't really more active than the chloride but barium is very much more active than sodium.

Dr U. Beck Please let me make a short comment on the experimental methods you mentioned. I want to draw your attention to a quite different method of measuring mobilities. This is in some ways a new method and it has some advantages over micro-electrophoresis. We use the Debye ultrasound effect following the work by Yeager, Zana *et al.* If you transmit pulsed ultrasonic waves into a solution which contains an electrolyte you get a displacement between the cations and anions. The same holds for colloidal suspensions, if the suspension contains electrolyte. This displacement between the charges can be detected by a small electrode of platinum wire. The measured 'vibration potential' is a relative measure of the zeta potential. You know probably the calculations by Booth and Enderbye on this effect. You get some advantages by this method. For instance, you are not limited in particular sizes or concentrations. You even get some information about the double layer thickness if you vary the frequency of the ultrasound, you

Under the chairmanship of A. A. Robertson can even measure the Kerr effect very precisely and quickly. So I think this is a further method which can give information about mobilities, zeta potential and double layer problems which can't be tackled with other techniques.

Overbeek Thank you. I remember that A. J. Rutgers in the thirties tried to apply the ultrasonic vibration potential to colloidal systems. At that time he was successful in showing the sign and the presence of the effect but it wasn't really quantitative enough to do zeta potential measurements at that time.

Beck I believe the technique has now been developed so that it can be used quantitatively.

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